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Synthesis and X-ray structural studies of pentaborate(1-) salts containing substituted imidazolium cations.

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Abstract

The preparation of [NMC][B₅O₆(OH)₄] {NMC = 2-MeC₃N₂H₄ (**3**), 1-MeC₃N₂H₄ (**4**), 4-MeC₃N₂H₄ (**5**), 1,2-Me₂C₃N₂H₃ (**6**), 1,2,3-Me₃C₃N₂H₂ (**7**), 1-EtC₃N₂H₄ (**8**), 2-EtC₃N₂H₄ (**9**), 2-Et-4-MeC₃N₂H₃ (**10**), 1-Et-3-MeC₃N₂H₃ (**11**) and 2-ⁱPrC₃N₂H₄ (**12**)} salts are reported. Compounds were characterized by spectroscopy (NMR and IR) and by single crystal XRD (**6**, **7**, **9**, **10**, **12**) studies. All structures show extensive H-bonded networks and **7** displays the first example of reciprocal paired $\alpha\alpha\alpha$ anion-anion interactions. These are facilitated by the pentaborate boroxole rings being significantly distorted (boat) from the near-planar arrangements more commonly observed. The related imidazolium salt, [2-MeC₃N₂H₆][B₅O₆(OH)₄] (**13**), has also been characterized by XRD studies. Compound **13** is isostructural with **3**. Thermal properties (TGA/DSC) indicate decomposition to B₂O₃ *via* [NMC][(B₅O₈)_n] intermediates.

Keywords: borate; pentaborate; polyborate; imidazolium; X-ray structures; H-bonding.

1. Introduction

There are many known examples of polyborate salts with either metal or non-metal cations (NMCs), and they exhibit great structural diversity [1,2]. Polyborate anions are classified as either 'condensed', containing polymeric chains, layers, nets etc, or as 'isolated' with well defined anionic entities [3]. Both systems may be prepared from aqueous solution although more forcing conditions are often required for the condensed systems [4]. Within the isolated systems, polyborate anions containing three [5,6], four [7,8], five [9], seven [10-13], eight [14], nine [15,16], fourteen [17] and fifteen [18] B atoms have been obtained. Of these the [NMC][B₅O₆(OH)₄] salts are well-known (see below), but most other NMC polyborate salts are limited to just a few examples of each class. It is becoming increasingly apparent that crystalline polyborate products which are formed are more strongly influenced by H-bonding interactions and crystal packing forces than by reaction conditions/reactant stoichiometry since many polyborate species co-exist in aqueous solution as a consequence of rapidly attained equilibria [19,20].

Literature reports of nonaborate(3-) salts are limited to [C₃N₂H₅]₃[B₉O₁₂(OH)₆] (**1**) and [C(NH₂)₃]₃[B₉O₁₂(OH)₆] (**2**) which contain imidazolium(1+) and guanidinium(1+) cations, respectively [15,16]. As part of a continuing study relating to the thermal properties of NMC polyborates [6,13,21] we were interested in preparing more examples of these rare non-metal cation salts with nonaborate anions (Figure 1) and have investigated the synthesis of polyborate salts derived from related imidazolium cations. However, for the reason described above we were unable to isolate further examples of these nonaborate salts but we successfully prepared a number of salts containing pentaborate anions (Figure 1). The synthesis, characterization and thermal properties of these new pentaborate salts form the basis of this manuscript.

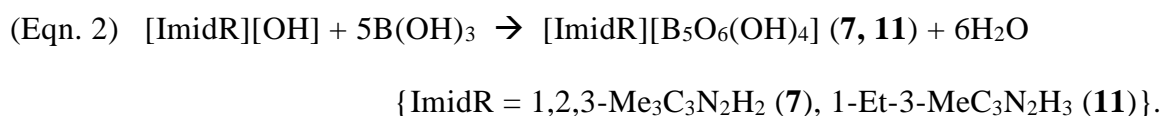
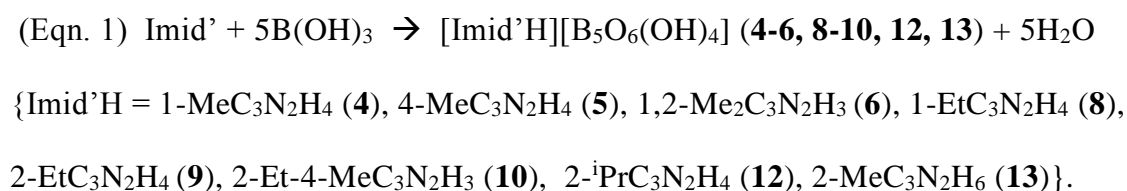
2. Results and Discussion

2.1 Synthesis and characterization

Characterization data reported for **1** and **2** are limited to single-crystal XRD studies and elemental analyses [15,16]. We successfully re-synthesised these two compounds by the literature method [15], with bulk samples of satisfactory elemental analysis data. Spectroscopic data for these compounds are discussed below and are reported in the experimental section. IR spectroscopic analysis has been described as an under-rated tool for polyborate structural analysis, and detailed literature assignments have been made for monoborate through to hexaborate species [22]. IR data for **1** (and **2**) are given in the experimental section and tentative B-O assignments for **1** can be made, by visual comparison with [Imid]Cl for elimination of imidazolium cation peaks. Compound **1** (and **2**) shows 3 peaks in the region 1300-1400 cm^{-1} , assigned to $\nu_{\text{as}}(\text{B}_{(3)}\text{-O})$, and a further strong signal centered at 1050 cm^{-1} , assigned as $\nu_{\text{as}}(\text{B}_{(4)}\text{-O})$. In addition, both compounds show bands at 943 cm^{-1} and 890 cm^{-1} , assigned as $\nu_{\text{s}}(\text{B}_{(3)}\text{-O})$, and the higher energy band of these two is sharper may be diagnostic of the $[\text{B}_9\text{O}_{12}(\text{OH})_6]^{3-}$. A band at 815 cm^{-1} , probably $\nu_{\text{s}}(\text{B}_{(4)}\text{-O})$, is also apparent in IR spectra of both compounds. It can be noted that the band which we have assigned as characteristic of $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ (~925 cm^{-1} [23]), and assigned to $\nu_{\text{s}}(\text{B}_{(3)}\text{-O})$, is present in **3-13**, and absent in **1** and **2**.

The attempted syntheses of a series substituted tris(imidazolium) nonaborate(3-) salts by Schubert's method (3:1 ratio, high temperature) were all unsuccessful and resulted in materials which were identified as substituted imidazolium pentaborate(1-) salts. The substituted imidazolium cations used in this study are illustrated in Figure 2. The products were obtained in low yields but increasing the $\text{B}(\text{OH})_3$:imidazole ratio to 5:1 resulted in the formation of these pentaborate(1-) salts in higher yields. This method has

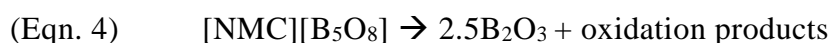
been previously used to prepare [2-MeC₃N₂H₄][B₅O₆(OH)₄] (**3**) and other non-metal cation pentaborate salts [21]. The unsubstituted imidazolium pentaborate, [C₃H₅N₂][B₅O₆(OH)₄] has been synthesized by a solvothermal method [24]. The new substituted imidazolium pentaborate salts **4-12**, synthesised according to Eqns 1 and 2 were obtained in reasonable yields and had satisfactory elemental analysis data. The related imidazolinium salt, [2-MeC₃N₂H₆][B₅O₆(OH)₄] (**13**), with a saturated cyclic ethane linkage, was also synthesized by the method in Eqn 1.



The ionic structures of **6, 7, 9, 10, 12** and **13** were confirmed by single-crystal X-ray studies (see section 2.3). Spectroscopic and thermal data are reported in the experimental section and NMR and IR data for the X-ray determined structures were in accord with their crystallographic structures and data for **3, 4, 5, 8, 11**, and **13** were comparable. ¹¹B NMR spectra showed peaks at +18, +13 and +1ppm consistent with equilibria linking monoborate/polyborate species [19,20] as has been observed before for pentaborates in aqueous solution [21]. ¹H and ¹³C NMR spectra were in accord with their formulated structures with NH and BOH protons producing a broad signal at ~+4.7ppm. IR spectra for all pentaborates showed the diagnostic band at ~925cm⁻¹ [23]. The ¹H and ¹³C NMR spectra of the cation in **13** is consistent with a 'planar' structure [25].

2.2 Thermal properties

The thermal decomposition properties (in air) of compounds **4-13** were studied by TGA and DSC. Heating samples in air to 1000°C resulted in dark glassy solids and the residual masses obtained were consistent with production of B₂O₃ from [B₅O₆(OH)₄]⁻. DSC traces indicated that the decomposition steps below 250°C were endothermic and those above 250°C were exothermic. This is consistent with previous observations [15,26,27], which have shown the thermal decomposition generally occur via a series of steps involving dehydration (endothermic) and oxidation (exothermic), as shown in Eqns 3 and 4.



2.3 XRD Structural studies

The formulated ionic structures of **6, 7, 9, 10, 12** and **13** were confirmed by single crystal XRD studies. Crystallographic data are given in Table 1 and full details are available in supplementary data. All structures contained the expected substituted imidazolium(1+) cations or the imidazolinium(1+) cation partnered with a pentaborate(1-) anion. All compounds showed extensive H-bonded anion-anion interactions and the cations in **6, 7** and **12** were disordered over 2 sites. Compound **6** was crystallized with 1 water of crystallization. The co-crystallization of small molecules such as H₂O or B(OH)₃ within the anionic lattice is not uncommon and these additional molecules serve as 'spacer' molecules which expand the H-bonded lattice [13,14,26,28].

Bond lengths and bond angles associated with the boroxole rings of the pentaborate anions found in **6, 9, 10, 12** and **13**, are generally in accord with literature data for other

[NMC][B₅O₆(OH)₄] structures [21,26,29,30] and do not significantly differ from organo-substituted boroxole ring systems [31-33] containing both 3- and 4-coordinate B atoms bound to O. These structures need no further comment other than noting that the H bond interactions arising from the pentaborate donor sites are $\alpha\alpha\beta\omega$ for **6** and $\alpha\alpha\alpha\beta$ for **9**, **10**, **12** and **13**, where α and β are pentaborate acceptor sites, and ω is an H₂O acceptor site [13,14]. In all cases the α -interactions are through R₂²(8) reciprocal pairs [34]. The $\alpha\alpha\alpha\beta$ motif is commonly observed in herringbone or brickwall structures [14,21] and compound **9** has a herringbone structure. The C(8) β -interaction for **9** is shown in Figure 3. The β -interactions in **10** and **12** are through R₂²(12) reciprocal pairs (Figure 4), rather than the C(8) interactions. The cations in **3** and **13** have very similar volumes and steric requirements and differ by only 2H atoms, and as a result the crystallographic data for **13** is very similar to that which has been previously reported for **3** [21]. The imidazolium ring in **13** is crystallographically planar with eclipsed H atoms at saturated carbons with a C-C distance of 1.529(2)Å which is significantly longer than the distance found in the imidazolium salt **3** (1.328(4)Å) [21] and the other substituted imidazolium compounds reported here, 1.336(8)-1.350(6)Å. Compound **13** (and **3**) have $\alpha\alpha\alpha\beta$ configurations with the imidazolium cations bridging two pentaborates at β -acceptor sites *via* two donor H-bonds.

A drawing of the structure of **7** is shown in Figure 5. The anions link in a giant H-bonded lattice and their method of linkage ($\alpha\alpha\alpha\alpha$) is unusual and has not been observed previously. The cations, which are unable to participate in H-bonding, sit within the anionic lattice, and in order to accommodate the $\alpha\alpha\alpha\alpha$ configuration, the boroxole rings of the pentaborate(1-) anions are significantly distorted from the near-planar arrangements more commonly seen. A view of the H-bonded interactions for **7** around each pentaborate anion is shown in Figure 6. Both boroxole rings of the pentaborate

anion are in boat conformations as evidenced by the central B1 atom and the transannular O2 atom of one ring being 0.353 and 0.111 Å above the least square plane for O1B2O3B3, with the hydroxyl O atoms O7 and O8 below the plane by 0.104 and 0.183 Å, respectively. Similarly, B1 and transannular O5 are located 0.368 and 0.128 Å above the least square plane of O4B4O6B5, with the hydroxyl O atoms (O9 and O10) below this plane by 0.188 and 0.152 Å respectively. More importantly, O5 is located 1.519 Å above the plane of O1B2O3B3 (in other boroxole ring), and O2 is 1.596 Å above the plane of O4B4O6B5 (other boroxole ring), confirming a significant twist to the anion, since these would be expected to be within these planes in a non-distorted system. Despite the significant twist to the pentaborate structures the boroxole ring B-O bond lengths [1.351(3)-1.392(3) Å B(sp²); 1.464(3)-1.482(3) Å B(sp³)], OBO angles [109.7(2)-110.6(2)°, B(sp³); 115.4(2)-123.9(3)°, B(sp²)] and BOB angles [119.1(2)-112.0(2)°] remain within the normal ranges associated with pentaborate systems [14,21,29,30], including **6**, **9**, **10**, **12** and **13**.

3. Experimental

3.1 General

Chemicals were commercially available and used as supplied. NMR spectra were obtained on a Bruker Avance-500 spectrometer using XWIN-NMR 3.5. ¹¹B, ¹H and ¹³C spectra were obtained on samples dissolved in D₂O at 160, 500, and 125 MHz, respectively. FTIR spectra were obtained as KBr pellets on a Perkin-Elmer 100FTIR spectrometer. TGA and DSC were performed on an SDT Q600 instrument using Al₂O₃ crucibles with a ramp rate of 10°C per minute (RT to 1000°C in air). X-ray crystallography was performed at the EPSRC national crystallography service centre at Southampton University. CHN analyses were obtained from OEA Laboratories

(Callingham, Cornwall). Compounds **1**, **2** and **3** were obtained by a literature procedures [15,21]. The syntheses of the new pentaborate salts (**4-13**) are all very similar and representative methods are given for **4** and **7** below.

3.2 Synthesis, spectroscopic, thermal and analytical data

3.2.1 *Imidazolium nonaborate* [15], $[C_3N_2H_5]_3[B_9O_{12}(OH)_6]$, (**1**). Yield = 1.5g, 36% from 3.6g $B(OH)_3$. XRD: [d-spacing/Å (% rel. int.)]: 6.94 (100), 3.58 (93), 3.49 (75), 3.90 (52), 3.81 (51). Elemental anal. Calc. for $C_9H_{21}B_9O_{18}N_6$: C 18.1%, H 3.5%, N 14.0%. Found: C 18.2%, H 3.6%, N 14.0%. 1H /ppm: 4.7 (12H), 7.05 (6H, s), 7.92 (2H, s). ^{13}C /ppm 120.81 (2CH), 135.06 (CH). ^{11}B /ppm: 1.1 (<1%), 13.2 (5%), 18.1 (95%). IR (KBr/cm $^{-1}$): 3366(m), 3271(m), 3159(m), 2998(m), 2854(m), 1591(m), 1386(s), 1348(s), 1303(s), 1189(m), 1131(m), 1108(s), 1056(s), 996(m), 942(m), 887(s), 815(m), 778(m), 750 (m), 702 (m), 628 (s), 477 (m). TGA: loss of H_2O at 190°C, 12.1% (12.0% calc for $4H_2O$); residue at 700°C 56.0% (52% calc for $4.5B_2O_3$).

3.2.2 *Guanidinium nonaborate* [15], $[C(NH_2)_3]_3[B_9O_{12}(OH)_6]$, (**2**). Yield = 3.1g, 82% from 3.7g $B(OH)_3$. XRD: [d-spacing/Å (% rel. int.)]: 3.56 (100), 4.41 (22.7), 3.47 (13.9), 4.96 (13.0), 4.03 (10.2). Elemental. anal. Calc. for $C_3H_{24}B_9O_{18}N_9$: C 6.3%, H 4.23%, N 22.1%; Found: C 6.4%, H 4.5%, N 22.1%. 1H /ppm: 4.7 (br). ^{13}C /ppm: 154.4. ^{11}B /ppm: 13.7. IR (KBr/cm $^{-1}$): 3432(s), 3197(s), 1686(s), 1655(s), 1571(m), 1405(s), 1351(s), 1294(s), 1216(w), 1145(m), 1130(m), 1052(s), 1031(s), 945(m), 895(m), 814(m), 755(w), 700(m), 526(m). TGA: loss of H_2O at 250°C, 19.0% (18.9% calc for $6H_2O$); residue at 700°C 53.0% (54.8% calc for $4.5B_2O_3$).

3.2.3 *1-Methylimidazolium pentaborate*, $[1-MeC_3N_2H_4][B_5O_6(OH)_4]$, (**4**). $B(OH)_3$ (7.43g, 121.80mmol) was dissolved in a warm MeOH/ H_2O (100ml, 1:1) 100ml. 1-Methylimidazole (2.00g, 24.36mmol) was added to the solution which was warmed for 1h. The solvent was removed by rotary evaporation and the resulting solid was dried at

110°C for 24h to yield product as a white solid (7.03g, 96%). Elemental anal. Calc for $C_4H_{11}B_5N_2O_{10}$: C 16.0%, H 3.7%, N 9.3%. Found: C 16.0%, H 3.7%, N 9.2%. 1H /ppm: 3.75 (3H, s), 4.71 (5H, s), 7.2 (2H, s), 8.27 (1H, s). ^{13}C /ppm: 34.1 (CH₃), 120.7 (CH), 121.8 (CH), 135.0 (CH). ^{11}B /ppm: 1.1, 13.0, 18.6. IR (KBr/cm⁻¹): 3379(vs), 3113(m), 1435(vs), 1360(vs), 1103(s), 1026(s), 926(s), 782(m), 697(m), 626(w). TGA: loss of H₂O 15.0% (11.9% calc); residual B₂O₃ 57.0% (57.8% calc).

3.2.4 4-Methylimidazolium pentaborate, [4-MeC₃N₂H₄][B₅O₆(OH)₄], (5). Method as **4**, yield = 7.1g, 96% from 7.43g B(OH)₃. Elemental anal. Calc for $C_4H_{11}B_5N_2O_{10}$: C 15.9, H 3.7, N 9.3%. Found: C 16.4%, H 3.7%, N 9.4%. 1H /ppm: 2.15 (3H, s), 6.92 (1H, s), 4.7 (5H), 8.16 (1H, s). ^{13}C /ppm: 9.1 (CH₃), 116.0 (CH), 130.0 (C), 132.9 (CH). ^{11}B /ppm: 1.1, 13.1, 18.5. IR (KBr/cm⁻¹): 3166(s), 1634(m), 1420(vs), 1309(vs), 1164(s), 1084(m), 1032(m), 916(s), 823(m), 777(m), 699(s), 623(m). TGA: loss of H₂O 15.0% (11.9% calc); residual B₂O₃ 57.0% (57.8% calc).

3.2.5 1,2-Dimethylimidazolium pentaborate, [1,2-Me₂C₃N₂H₃][B₅O₆(OH)₄], (6). Method as **4**, yield = 6.21g, 95% from 6.43g B(OH)₃. Elemental anal. Calc for $C_5H_{13}B_5N_2O_{10}$: C 19.0, H 4.2, N 8.9%. Found: C 19.3%, H 4.2%, N 8.8%. 1H /ppm: 2.42 (3H, s), 3.60 (3H, s), 4.70 (5H, s), 7.09 (2H, s). ^{13}C /ppm: 10.0 (CH₃, s), 33.5 (CH₃, s), 118.7 (CH, s), 122.4 (CH, s), 144.7 (C) ^{11}B /ppm: 1.1, 13.2, 18.8. IR (KBr/cm⁻¹): 3391(vs), 3087(s), 1621(w), 1440(vs), 1341(vs), 1103(s), 1026(s), 925(s), 782(m), 697(m). TGA: loss of H₂O 15.0% (16.2% calc); residual B₂O₃ 52.0% (52.2% calc). Recrystallisation from H₂O yielded crystals of **6**.H₂O suitable for XRD studies.

3.2.6 1,2,3-Trimethylimidazolium pentaborate, [1,2,3-Me₃C₃N₂H₂][B₅O₆(OH)₄], (7). 1,2,3-trimethylimidazolium iodide (4.00g, 16.80mmol) was dissolved in water (50ml) and Dowex 550A monosphere (OH⁻ form) was added and the suspension was stirred for 24h. The ion exchange resin was removed by filtration and methanol (50ml) was added to the

filtrate. Boric acid (5.19g, 84.01mmol) was added to the filtrate and the solution was heated for 1h. The solvent was removed by rotary evaporation and solid was dried at 110°C for 24h to yield a pale orange solid (4.31g, 78%). Elemental anal. Calc for C₆H₁₅B₅N₂O₁₀: C 21.9, H 4.6, N 8.5%. Found: C 21.4%, H 4.6%, N = 7.8%. ¹H/ppm: 2.45 (3H, s), 3.65 (6H, s), 4.7 (4H), 7.17 (2H, s). ¹³C/ppm: 8.6 (CH₃), 34.5 (2 x CH₃), 121.7 (2 x CH), 144.6 (C). ¹¹B/ppm: 1.2, 13.0, 19.0. IR (KBr/cm⁻¹): 3378(vs), 3231(vs), 1436(vs), 1358(vs), 1255(m), 1104(m), 1025(m), 923(s), 782(m), 713(w), 652(w). Recrystallisation from H₂O yielded crystals of **7** suitable for XRD studies.

3.2.7 *1-Ethylimidazolium pentaborate, [1-EtC₃N₂H₄][B₅O₆(OH)₄], (8)*. Method as **4**, yield = 7.06g, 96% from 6.43g B(OH)₃. Elemental anal. Calc for C₅H₁₃B₅N₂O₁₀: C 19.0, H 4.2, N 8.9%. Found: C 18.9%, H 4.3%, N 8.6%. ¹H/ppm: 1.35 (3H, t, *J* = 7.25Hz), 4.06 (2H, q, *J* = 7.25Hz), 4.7 (5H), 7.17 (1H, s), 7.26 (1H, s), 8.23 (1H, s). ¹³C/ppm: 14.8 (CH₃), 46.6 (CH₂), 120.8 (CH), 122.1 (CH), 134.9 (CH). ¹¹B/ppm: 18.6. IR (KBr/cm⁻¹): 3380(vs), 3072(s), 1440 (vs), 1356(vs), 1258(m), 1102(s), 1025(s), 925(s), 782(m), 696(m). TGA: loss of H₂O 13.0% (11.4% calc); residual B₂O₃ 53.5% (55.2% calc).

3.2.8 *2-Ethylimidazolium pentaborate, [2-EtC₃N₂H₄][B₅O₆(OH)₄], (9)*. Method as **4**, yield = 6.32g, 96% from 6.46g B(OH)₃. Elemental anal. Calc for C₅H₁₃B₅O₁₀N₂: C 19.1%, H 4.2%, N 8.9%. Found: C 19.4%, H 4.2%, N 8.9%. ¹H/ppm: 1.19 (3H, t, *J* = 7.5Hz), 2.79 (2H, q, *J* = 7.5Hz), 4.7 (6H), 7.09 (2H, s). ¹³C/ppm: 10.6 (CH₃), 19.2 (CH₂), 118.8 (2 x CH), 149.4 (C). ¹¹B/ppm: 1.1, 13.2, 18.9. IR (KBr/cm⁻¹): 3350(s), 2995(m), 1624(m), 1399(vs), 1311(vs), 1198(m), 1136(m), 928(vs), 776(m), 701(m). TGA: loss of H₂O 15.0% (11.4% calc); residual B₂O₃ 56.0% (55.2% calc). Recrystallisation from H₂O yielded crystals of **9** suitable for XRD studies.

3.2.9 *2-Ethyl-4-methylimidazolium pentaborate, [2-Et-4-MeC₃N₂H₃][B₅O₆(OH)₄], (10)*. Method as **4**, yield = 5.51g, 92% from 5.61g B(OH)₃. Elemental anal. Calc for

$C_6H_{15}B_5N_2O_{10}$: C 21.9%, H 4.6%, N 8.5%. Found: C = 22.3%, H 4.6%, N 8.3%. 1H /ppm: 1.18 (3H, t, $J = 7.75$ Hz), 2.12 (3H, s), 2.76 (2H, q, $J = 7.75$ Hz), 4.7 (6H), 6.79 (1H, s). ^{13}C /ppm: 9.0 (CH₃), 10.5 (CH₃), 19.1 (CH₂), 114.6 (CH), 129.2 (C), 148.3 (C). ^{11}B /ppm: 1.1, 13.0, 18.6. IR (KBr/cm⁻¹): 3420(vs), 3143(s), 1407(vs), 1318(vs), 1196(w), 1078(m), 1027(m), 926(s), 776(m), 706(w). TGA: loss of H₂O 10.0% (9.7% calc); residual B₂O₃ 41.0% (43.4% calc). Recrystallisation from H₂O yielded crystals of **10** suitable for XRD studies.

3.2.10 1-Ethyl-3-methylimidazolium pentaborate, [1-Et-3-Me-C₃N₂H₃][B₅O₆(OH)₄], (11). Method as **7**, Yield = 3.09g, 90% from 3.24g B(OH)₃ and 1-ethyl-3-methylimidazolium bromide. Elemental anal. Calc for $C_6H_{15}B_5N_2O_{10}$: C 21.9%, H 4.6%, N 8.5%. Found: C 21.7%, H 4.6%, N 8.2%. 1H /ppm: 1.29 (3H, t, $J = 7.7$ Hz), 4.12 (2H, q, $J = 7.7$ Hz), 4.39 (3H, s), 4.7 (4H), 7.75 (2H, s), 8.92 (1H, s). ^{13}C /ppm: 15.20 (CH₃), 37.0 (CH₃), 42.0 (CH₂), 122.8 (2 x CH), 137.0 (C). ^{11}B /ppm: 1.1, 13.3, 18.9. IR (KBr/cm⁻¹): 3230(s), 3020(s), 1440(vs), 1357(s), 1255(s), 1110(m), 1025(m), 925(s), 780(m), 710(m). TGA: loss of H₂O 13.0% (10.9% calc); residual B₂O₃ 57.5% (52.5% calc).

3.2.11 2-Isopropylimidazolium pentaborate, [2-ⁱPr-C₃N₂H₄][B₅O₆(OH)₄], (12). Method as **4**, yield = 5.51g, 92% from 5.61g B(OH)₃. Elemental anal. Calc for $C_6H_{15}B_5N_2O_{10}$: C 21.9%, H 4.6%, N 8.5%. Found: C 22.3%, H 4.6%, N 8.6%. 1H /ppm: 1.22 (6H, d, $J = 6.9$ Hz), 3.13 (1H, sept, $J = 6.9$ Hz), 4.7 (6H), 7.08 (2H, s). ^{13}C /ppm: 19.7 (2 x CH₃), 26.6 (CH), 118.9 (2 x CH), 153.1 (C). ^{11}B /ppm: 1.1, 13.2, 18.9. IR (KBr/cm⁻¹): 3414(s), 3147(s), 3021(s), 2932(m), 1623(m), 1405(vs), 1316(vs), 1184 (m), 1067(m), 1023(m), 917(s), 777(m), 719(m). Recrystallisation from H₂O yielded crystals of **12** suitable for XRD studies. TGA: loss of H₂O 15.0% (10.9% calc); residual B₂O₃ 51.0% (52.9% calc).

3.2.12 2-Methyl-2-imidazolinium pentaborate, [2-Me-C₃N₂H₆][B₅O₆(OH)₄], (13). Method as **4**, yield 7.02g (97%) from 7.35g B(OH)₃. Elemental anal. Calc for

C₄H₁₃B₅N₂O₁₀: C 15.8%, H 4.3%, N 9.2%. Found: C 15.9%, H 4.5%, N 9.1%. ¹H/ppm: 1.87 (3H, s), 3.34 (4H, s), 4.7 (6H, s). ¹³C/ppm: 11.6 (CH₃), 44.3 (2 x CH₂), 168.5 (C). ¹¹B/ppm: 1.1, 13.1, 18.9. IR (KBr/cm⁻¹): 3381(s), 1619(m), 1432(vs), 1180(m), 1025(s), 922(vs), 779(m), 704(m), 583(w). TGA: loss of H₂O 15.0% (11.8% calc); residual B₂O₃ 55.0% (57.0% calc). Recrystallisation from H₂O yielded crystals of **13** suitable for XRD studies.

3.3 X-ray crystallography

The crystallographic data collection of compounds **6**, **7**, **10**, **12** and **13** were performed using a Nonius Kappa CCD diffractometer with Mo K_α radiation ($\lambda = 0.71073\text{\AA}$) controlled by the Collect [35] software package and an Oxford Cryosystem N₂ open flow cryostat at 120(2) K. The data were processed using Denzo [36] and semi-empirical absorption corrections were applied using SORTAV [37,38]. The crystallographic data collection for compound **9** was performed on a Rigaku AFC12 diffractometer equipped with an enhanced sensitivity (HG) *Saturn724+* CCD detector mounted at the window of a FR-E+ SuperBright rotating anode generator (Mo K_α radiation ($\lambda = 0.71075\text{\AA}$)) equipped with VariMax HF (High Flux) optics at 100(2) K. Software package CrystalClear-SM Expert 2.0 r 13 [39] was used for the cell determination, data collection, integration, scaling and absorption correction. Crystallographic data are given in Table 1. The structures were solved by direct methods and refined by full-matrix least-square procedures on *F*² using SHELXS-97 and SHELXL-97 respectively [40]. All non-hydrogen atoms were refined anisotropically.

Crystallographic data for **6**, **7**, **9**, **10**, **12** and **13** have been deposited with the Cambridge Crystallographic Data Centre with CCDC971516-971521. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2

1EZ (fax +44 1223 336033) or email: deposit@ccdc.cam.ac.uk or www:
http://www.ccdc.cam.ac.uk.

4. Conclusions

A series of substituted-imidazolium(1+) pentaborate(1-) salts have been prepared. IR spectra can be used to differentiate between the imidazolium nonaborate (**1**) and related pentaborates (**3-13**). The compounds characterized by single-crystal XRD (**6, 7, 9, 10, 12** and **13**) all show extensive three dimensional H-bonded lattices. The first example of reciprocal-paired $\alpha\alpha\alpha$ anion-anion interactions is observed in **7** where, in order to accommodate these interactions, the pentaborate boroxole rings are significantly distorted away from planar towards boat conformations. The β interactions in **10** and **12** (both $\alpha\alpha\beta$) are through reciprocal paired $R_2^2(12)$ interactions rather than the more common C(8) chain, observed in **9, 10**, and **13**. All substituted-imidazolium pentaborate salts are thermally decomposed in air *via* a multistage process to glassy B_2O_3 . Thermally derived materials were amorphous and non-porous.

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FIGURES

Figure 1

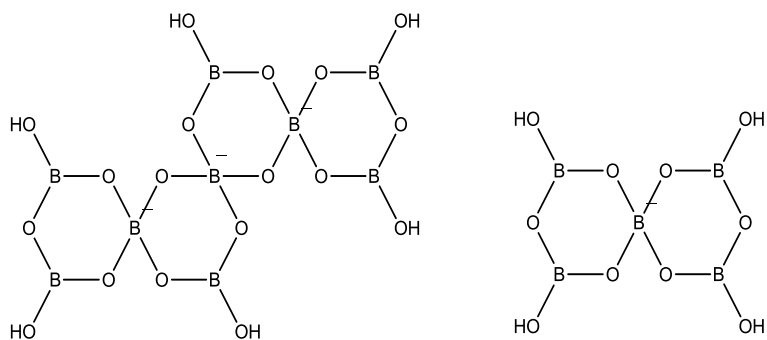
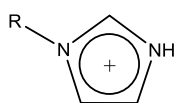
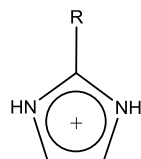


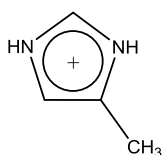
Figure 2



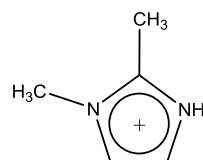
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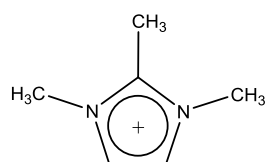
R = CH₃ (3), C₂H₅ (9), ⁱPr (12)



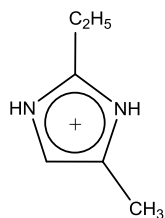
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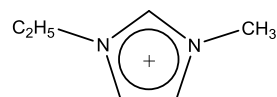
(6)



(7)



(10)



(11)

Figure 3

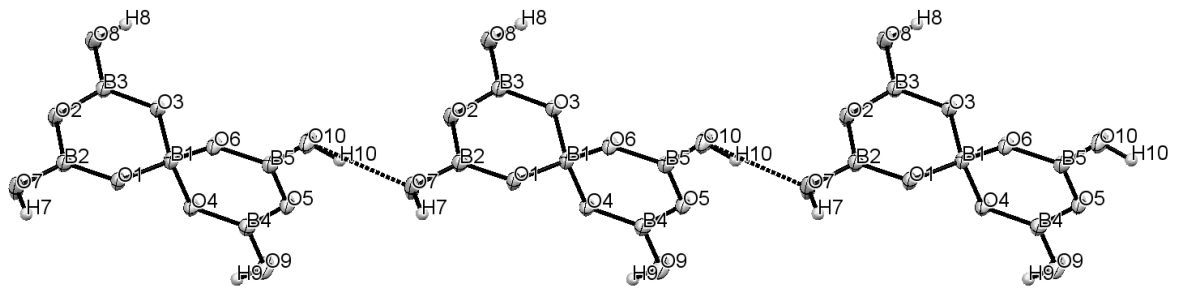


Figure 4

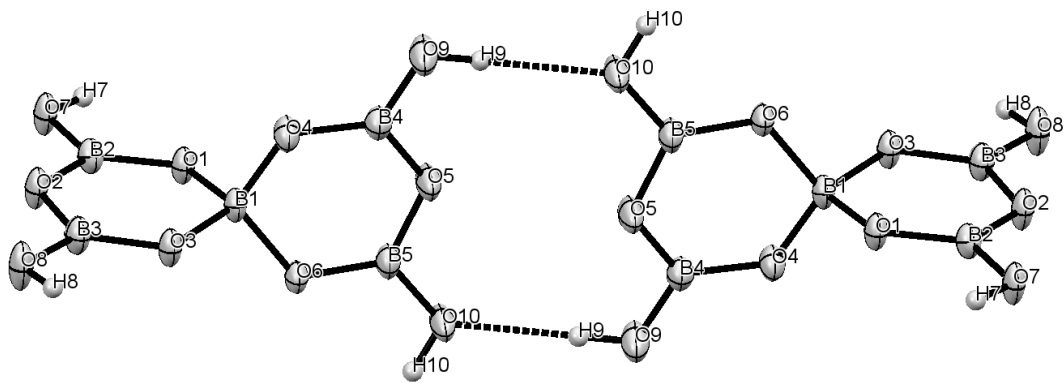


Figure 5

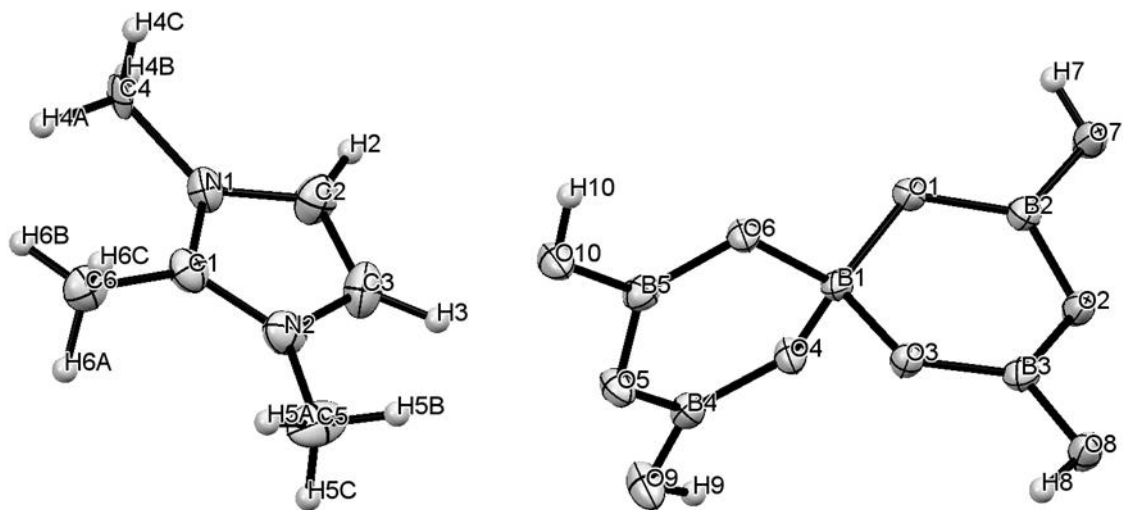
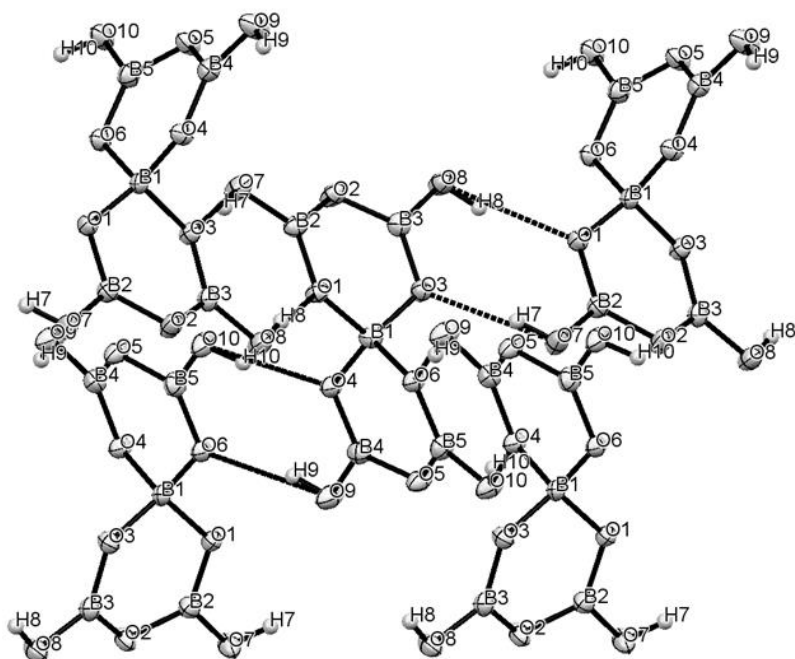


Figure 6



Captions to Figures

Figure 1

Schematic drawings of nonaborate(3-) (left) and pentaborate(1-) (right) anions observed in **1,2** and **3-13**, respectively.

Figure 2

Schematic drawings of the imidazolium cations partnered with pentaborate anions in **3-12**. Elsewhere in the manuscript these compound numbers refer to the [NMC][B₅O₆(OH)₄] salts but the pentaborate anions are omitted for clarity in this Figure.

Figure 3

H-bond interactions: the C(8) chain structure (β -interaction) as found in **9**. The H-bond data are $d(\text{H10}\dots\text{O7})$ 1.81 Å, $d(\text{O10}\dots\text{O7})$ 2.6285(15) Å, angle O10H10O7, 166.2°. Each pentaborate anion also forms 3 additional H-bond interactions to α -sites.

Figure 4

H-bond interactions: the R₂²(12) ring structure (β -interactions) as found in **12**. The H-bond data are $d(\text{H9}\dots\text{O10})$ 1.84 Å, $d(\text{O9}\dots\text{O10})$ 2.6708(18) Å, angle O9H9O10, 167.4°. Each pentaborate anion also forms 3 additional H-bond interactions to α -sites.

Figure 5

ORTEP drawing of [1,2,3-Me₃C₃N₂H₂][B₅O₆(OH)₄] (**7**) showing atomic numbering scheme. The cation is disordered over two sites and the one with highest s.o.f [0.641(7)] is shown. Selected boroxole ring parameters (bondlength, Å; angles, °) are: B1-O1 1.464(3), B1-O3 1.482(3), B1-O4 1.481(3), B1-O6 1.468(3), B2-O1 1.375(3), B2-O2 1.385(3), B2-O7 1.351(3), B3-O2 1.372(4), B3-O3 1.360(3), B3-O8 1.262(4); O1-B1-O3 109.93(19), B1-O3-B3 120.9(2), O3-B3-O2 121.0(2), B3-O2-B2 119.1(2), O2-B2-O1 120.4(2), B2-O1-B1 120.6(2).

Figure 6

Pentaborate lattice for **7** showing the $\alpha\alpha\alpha$ H-bond interactions (data arranged $d(\text{H}\dots\text{A})$ (Å), $d(\text{D}\dots\text{A})$ (Å), angle DHA (°): O7-H7...O3' (α) 1.84, 2.676(2), 170.2; O8-H8...O1'(α) 1.93, 2.745(3), 164.6; O9-H9...O6'(α) 1.92, 2.743(2), 167.0; O10-H10...O4'(α) 1.85, 2.676(2), 167.9.

TABLE

Table 1

Crystal	6	7	9	10	12	13
Empirical Formula	C ₄ H ₁₅ B ₃ N ₂ O ₁₁	C ₆ H ₁₅ B ₃ N ₂ O ₁₀	C ₅ H ₁₃ B ₃ N ₂ O ₁₀	C ₆ H ₁₅ B ₃ N ₂ O ₁₀	C ₆ H ₁₅ B ₃ N ₂ O ₁₀	C ₄ H ₁₃ B ₃ N ₂ O ₁₀
Formula wt/ g mol ⁻¹	333.24	329.25	315.22	329.25	329.25	303.21
Crystal System, space group	Triclinic, P-1	Orthorhombic, P2 ₁ 2 ₁ 2 ₁	Monoclinic, P2 ₁ /c	Triclinic, P-1	Triclinic, P-1	Monoclinic, P2 ₁ /c
a/Å	9.0508(2)	11.0588(4)	9.215(2)	8.5389(3)	8.1239(5)	8.3328(2)
b/Å	9.3334(2)	11.4508(2)	15.592(4)	8.9036(4)	9.4947(5)	11.3902(3)
c/Å	9.6600(5)	11.6188(3)	9.824(2)	9.9942(4)	9.9342(4)	13.8886(4)
α/°	104.873(1)	90	90	84.600(2)	106.587(3)	90
β/°	98.666(1)	90	90.137(5)	76.334(2)	91.279(3)	90.298(2)
γ/°	111.701(1)	90	90	89.095(2)	96.031(3)	90
Vol/Å ³	704.85(3)	1471.31(7)	1411.5(6)	735.02(5)	729.21(7)	1318.18(6)
Z, Calc density (Mgm ⁻³)	2, 1.570	4, 1.486	4, 1.483	2, 1.488	2, 1.500	4, 1.528
Abs coeff (mm ⁻¹)	0.141	0.129	0.131	0.129	0.130	0.137
F(000)	344	680	648	340	340	624
Crystal	Colourless block	Colourless cut block	Colourless cut block	Colourless slab	Colourless plate	Colourless cut block
Crystal Dimensions/mm ³	0.22 x 0.18 x 0.15	0.18 x 0.12 x 0.08	0.19 x 0.12 x 0.06	0.56 x 0.36 x 0.08	0.52 x 0.32 x 0.08	0.48 x 0.40 x 0.32
θ range (°)	3.41 – 27.48	3.10 – 27.48	3.30 – 27.48	3.26 – 27.48	3.18 – 27.48	3.37 – 27.48
No. of reflections collected	12803	10499	24203	15392	14787	14265
R _{int}	0.0355	0.0452	0.0270	0.0404	0.0421	0.0316
No. of data/restraints/parameters	3204 / 16 / 268	1918 / 19 / 279	3230 / 0 / 204	3356 / 0 / 214	3347 / 24 / 271	3010 / 0 / 196
Final R indices [<i>F</i> ² > 2σ(<i>F</i> ²): R ₁ , wR ₂]	0.0377, 0.0861	0.0420, 0.0903	0.0413, 0.1077	0.0400, 0.0960	0.0549, 0.1452	0.0358, 0.0889
R indices (all data) : R ₁ , wR ₂	0.0444, 0.0912	0.0476, 0.0946	0.0458, 0.1109	0.0508, 0.1022	0.0720, 0.1578	0.0440, 0.0938
Largest diff. peak and hole/e Å ⁻³	0.200, -0.238	0.210, -0.241	0.402, -0.567	0.268, -0.259	0.566, -0.437	0.370, -0.226

Caption for Table 1

Crystal data and structure refinement for **6, 7, 9, 10, 12** and **13**.